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Thermal expansion at the incommensurate phase transition in $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ crystals

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Abstract

The temperature dependence of the thermal expansion in the vicinity of the incommensurate phase transition in $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ mixed crystals is found to deviate from that predicted within the Landau theory of phase transitions. It is shown that the dominant contribution to this deviation in the immediate vicinity of T_i is due to the presence of defects. The character of the deviation is found to be in qualitative agreement with the theoretically predicted behaviour in the presence of random field type defects. In some compounds ($x = 0, 2.4, 2.9$), the temperature dependence of the thermal expansion coefficient at $T \geqslant T_i + 3$ K can be described by a τ^{α}-dependence with $\alpha = 0.5$. These values are in reasonable agreement with $\alpha = 0.5$, corresponding to the fluctuation correction to the Landau theory. In solid solutions with a rather smeared paraelectric–incommensurate phase transition ($x = 0.25, 0.45$), the value of this exponent is found to be between 0.8 and 0.9. This suggests that the contribution to the thermal expansion due to the defects in these crystals is, even quite far from the phase transition, comparable to the contribution due to order parameter fluctuations.

1. Introduction

Among the A_2BX_4-type of crystals, the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ solid solutions have received considerable attention during the last decade. Its x–T phase diagram contains several critical points with various phase sequences. The pure bromide compound and rich bromide solid solutions undergo a second-order ferroelastic phase transition from an orthorhombic (space group Pnma) to a mono-clinic (space group $P112_1/a$) structure. At $x \approx 3.2$, the ferroelastic phase transition line splits into a second-order incommensurate and a first order lock-in phase transition. The incommensurate phase is characterized by a modulation wave vector $\boldsymbol{q} = (1/3 + \delta)\boldsymbol{a}^*$. At the triple point where the paraelectric–ferroelastic, paraelectric–incommensurate and incommensurate–ferroelastic phase transition lines converge, modulation wave vector changes discontinuously to its commensurate value $\boldsymbol{q}_0$ [1,2]. In the chloride-rich region of the $x - T$ phase diagram, a second incommensurate phase exists with modulation wave vector $\boldsymbol{q} = (2/5 + \delta)\boldsymbol{a}^*$. In addition to this, a commensurate ferroelastic phase with a fivefold unit cell is observed in a narrow temperature region. With decreasing temperature a phase transition into a ferroelastic phase takes place, characterized by a $P2_1/n11$ space group. Up to now, most studies have concentrated on the pure compounds. The aim of this paper is to

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study behaviour of the order parameter in the vicinity of the incommensurate phase transition throughout the phase diagram of the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ solid solutions. This has been accomplished by a study of the temperature dependence of the thermal expansion in several representatives of the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ solid solutions.

2. Experimental results

The crystals used in the experiments are grown from a seed in an aqueous solution of a stoichiometric mixture of $[N(CH_3)_4]Y$ and ZnY_2 (Y = Cl,Br) by a slow convection method. [3] In this way, large (1 cm^3) transparent crystals are obtained. The values x of the bromide concentration quoted throughout this paper are those of the growth solutions. The actual bromide concentrations in the crystals are expected to be somewhat higher than that of the growth solution. Raman spectroscopy experiments on the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ solid solutions have shown that these compounds have homogeneous Cl,Br distribution [4].

The thus obtained crystals have been unambiguously oriented by comparing their experimental morphology, measured using a goniometer, to the calculated theoretical morphology. For the

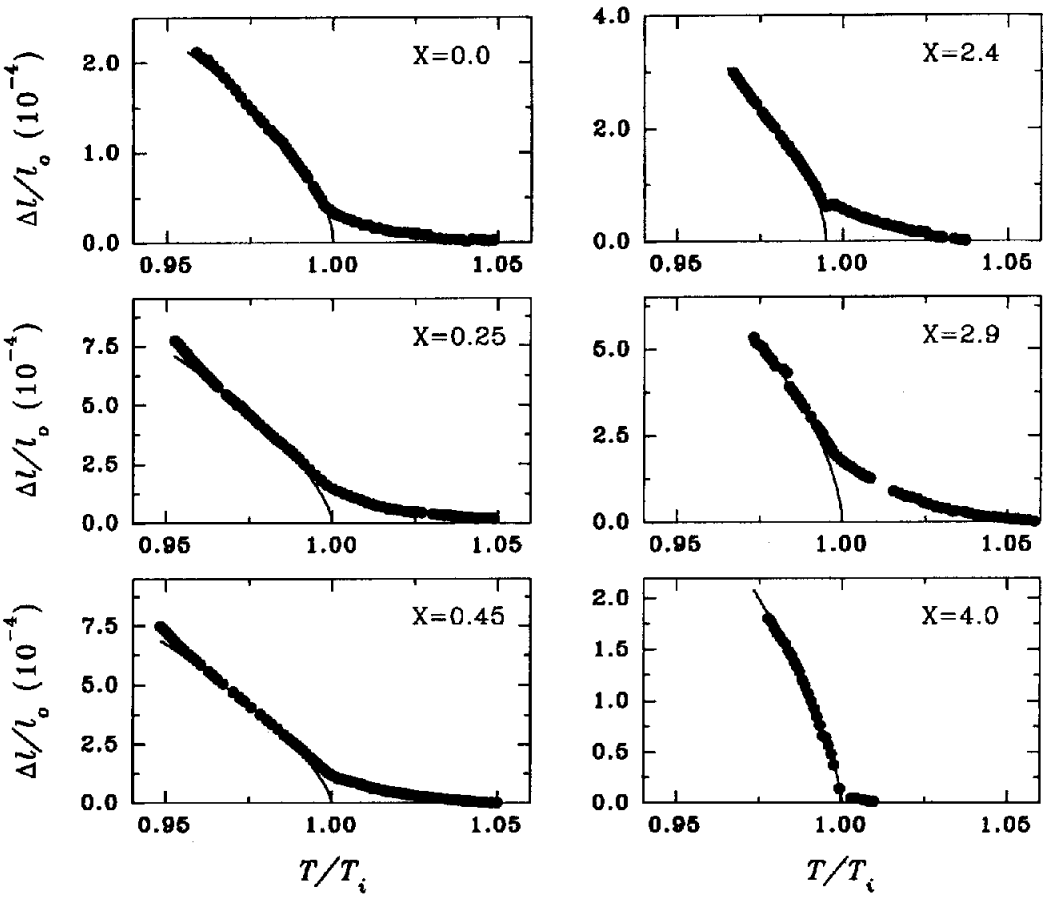

Fig. 1. Temperature dependence of the thermal expansion along the c-direction (dots) in $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ compounds in the vicinity of the incommensurate (x = 0, 0.25, 0.45, 2.4, 2.9) and ferroelastic (x = 4) phase transition after subtraction of a linear temperature dependence extrapolated from the high temperature data. The full lines show a fit of a $|\tau|^{2\beta}$ behaviour to the experimental data in the incommensurate (x = 4: ferroelastic) phase.

dilatometric measurements, the crystals were cut to obtain bars with a typical linear dimension of 5 to 8 mm along the c-axis. The samples were mounted into a copper cavity which was attached to the cold finger of a flow cryostat. The thermal expansion has been measured by means of a capacitance dilatometer with a 1 nm resolution. The measurements were carried out in the quasi-static regime during cooling with a temperature variation rate of about 0.2 K/min.

Fig. 1 shows the temperature dependence of the thermal expansion $\Delta l/l_0$ in the vicinity of the paraelectric–incommensurate phase transition for $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ crystals with $x = 0$, 0.25, 0.45, 2.4 and 2.9, as well as the thermal expansion in

Table 1
Phase transition temperatures observed in the thermal expansion experiments on $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ compounds with $x = 0$, 0.25, 0.45, 2.4, 2.9 and 4. T_i gives the transition temperature for the incommensurate phase transition, T_l for the lock-in phase transition, and T_c for the commensurate phase transition. The last two columns give the exponents α and 2β in the paraelectric and incommensurate phase, respectively

x	T_i (K)	T_l (K)	T_c (K)	α	β
0.0	297.3	281.3	277.0	0.59 ± 0.05	0.67
0.25	293.7	288.7	285.4	0.90 ± 0.05	0.66
0.45	293.2	277.1	—	0.84 ± 0.05	0.69
2.4	284.4	275.8	—	0.53 ± 0.05	0.68
2.9	279.1	270.0	—	0.55 ± 0.05	0.64
4.0	—	—	288.5	—	0.68

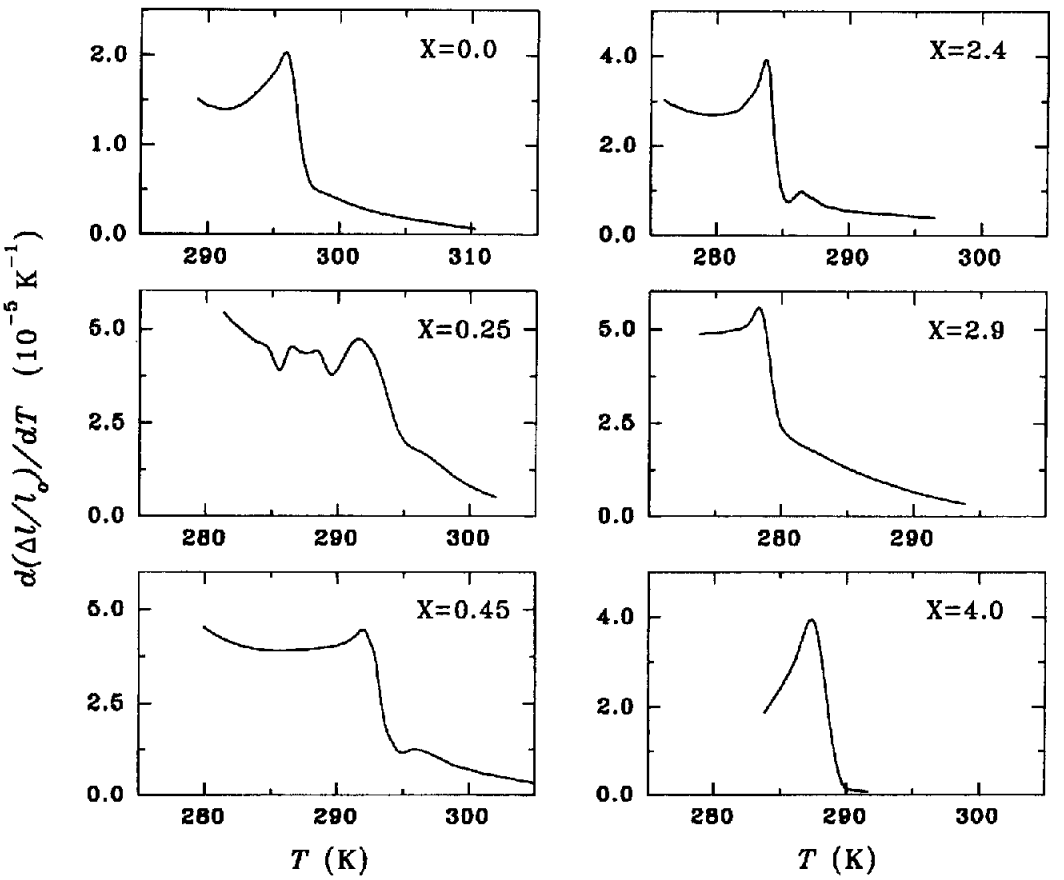

Fig. 2. Temperature dependence of the thermal expansion coefficient along the c-direction in the vicinity of the incommensurate ($x = 0$, 0.25, 0.45, 2.4, 2.9) and ferroelastic ($x = 4$) phase transition, obtained by taking the derivative of the thermal expansion data presented in Fig. 1 (after smoothing).

the vicinity of the paraelectric–ferroelastic phase transition in the pure bromide compound. These curves, plotted versus the reduced temperature T/T_i, are obtained by subtracting a linear background, extrapolated from the linear temperature dependence of $\Delta l/l_0$ in the high temperature phase. The corresponding phase transition temperatures can be found in the second column of Table 1. As is clear from the figure, a pronounced tail of the spontaneous deformation is observed above the phase transition temperature, which extends up to 15 K above T_i. The origin of this precursor effect is at present unclear, although it may be attributed to order parameter fluctuations or to effects due to the presence of defects. It is worth noting, however, that this deviation from the linear behaviour in the high temperature phase is found to be much smaller for the pure bromide compound, indicating that this precursor effect may be related to the existence of the incommensurate phase in the compounds $x < 3.2$, including the pure chlorine compound. The temperature dependence of $\Delta l/l_0$ exhibits a distinct bend at the phase transition. Below the phase transition $\Delta l/l_0$ shows a pronounced non-linear behaviour.

Fig. 2 shows the temperature dependence of the thermal expansion coefficient, obtained by taking the derivative of the smoothed experimental $\Delta l/l_0$ data shown in Fig. 1, for compounds with $x = 0$, 0.25, 0.45, 2.4, 2.9 and 4.0. The paraelectric–incommensurate and paraelectric–ferroelastic phase transitions are found as strong, broad peaks in the curves. Apart from this phase transition, the pure chloride compound shows, upon decreasing temperature, two additional jumps in the spontaneous deformation, corresponding to the first-order lock-in phase transition to the commensurate ferroelectric phase, and subsequent ferroelectric–ferroelastic phase transition, respectively. As expected, also the $x = 0.25$ compound shows both these phase transitions, as can be seen in Fig. 2 by the two small dips in the thermal expansion coefficient. Fig. 3 shows the temperature dependence of the thermal expansion for $x = 0$ and $x = 0.25$ in the vicinity of the ferroelectric phase. Contrary to the pure chloride compound the anomalies related to the phase transitions bounding the ferroelectric phase in the $x = 0.25$ solid solution are very weak.

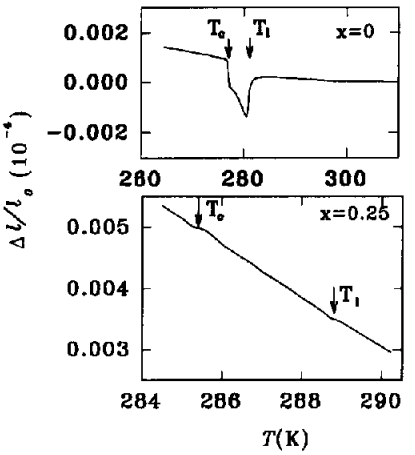

Fig. 3. Temperature dependence of the thermal expansion in $x = 0$ and $x = 0.25$ compounds in the vicinity of the ferroelectric phase.

This is very likely due to a smearing of the above phase transitions in the $x = 0.25$ solid solution by defects originating from the structural disorder.

The observed phase transition temperatures in the various compounds, gathered in Table 1, show a good agreement with the $x - T$ phase diagram reported by Colla and coworkers [2].

3. Discussion

To account for the interaction between the order parameter η and the deformation U of the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ crystals, one can include a term of the form $\eta\eta^* U$ in the thermodynamical potential expansion [5]. The form of this additional term suggests that the spontaneous deformation arising at the paraelectric–incommensurate phase transition has an order parameter dependence similar to that of the birefringence, i.e. it is a square function of the order parameter:

$$U \propto \Delta l/l_0 = Q\langle\eta^2\rangle, \tag{1}$$

where Q is the electrostriction coefficient, and $\langle\eta^2\rangle$ the average of the squared order parameter. For the non-critical region (not very close to the phase transition), the order parameter fluctuations near the phase transition can be accounted for within

the framework of the Landau theory by a small fluctuation correction. The temperature limit of the validity of the Landau theory is then given by the Ginzburg–Levanyuk criterion [6].

Apart from investigating the spontaneous deformation itself, it is also convenient to consider its temperature derivative $k = \mathrm{d}(\Delta l/l_0)/\mathrm{d}T$, since the thermal expansion coefficient k is expected to be far more sensitive to phase transitions. Besides that, it should be noted that the determination of a non-classical critical index β by describing the temperature dependence of the birefringence, or that of the spontaneous deformation, as $(T - T_i)^{2\beta}$ is questionable [7]. As in the case for the heat capacity and the temperature derivative of the birefringence [7], the temperature dependence of the thermal expansion coefficient can be described as

$$k^+ = k_b + \lambda^+ \tau^{-\alpha}, \quad \text{for } \tau > 0,$$

$$k^- = k_b + k_L + \lambda^- \tau^{-\alpha}, \quad \text{for } \tau > 0, \qquad (2)$$

where $\tau = (T - T_i)/T_i$, k_b is a background, and k_L is the jump of the thermal expansion coefficient at the phase transition in the Landau theory. The last term in these equations arises due to the correction to the Landau theory to account for order parameter fluctuations ($\alpha = 0.5$, $\lambda^-/\lambda^+ = 2\sqrt{2}$). The defect contribution in the non-critical region can also be described by a power law (Eq. (2)). [7] For various kinds of defects the α and λ^-/λ^+ parameters are different. For instance, random local field defects are characterized by $\alpha = 3/2$ and $\lambda^-/\lambda^+ = \sqrt{2}$ whereas random temperature type defects [8] do not change the character of the critical behaviour [8].

3.1. The paraelectric–incommensurate phase transition

The broad peaks observed at the second-order phase transition from the paraelectric phase show a strong asymmetry. The α exponents are found to differ drastically below and above the phase transition, and also the ratio between the prefactors, λ^-, λ^+, is found to differ from the value $2\sqrt{2}$ expected from the fluctuation correction to the Landau theory. In general, the temperature dependence of the thermal expansion coefficient is found to be much weaker in the incommensurate phase than it is in the high temperature phase. The asymmetrical broadening of the anomaly of k at the phase transition can be explained by the effect of the presence of local random field defects, which break down the long-range order in the incommensurate phase [9]. Qualitatively, the observed temperature dependence of the thermal expansion coefficient corresponds to the theoretically predicted temperature dependence due to the presence of random field type of defects [8]. This is also confirmed by the presence of the small, broad maximum in the thermal expansion coefficients of the compounds somewhat above the phase transitions. The similarity between the effects of the Cl/Br substitution with those of an external pressure [2,10] indicates that a random distribution of the substituted Br atoms may serve as a source for local random stress fields in these solid solutions.

On the high temperature side of the phase transition, sufficiently far away from T_i, where the amplitude of the defects contribution becomes rather small compared with the fluctuation correction, one would expect that the observed behaviour follows the Landau theory with the fluctuation correction, i.e. Eq. (2) with $\alpha = 0.5$. The validity range of this theory follows from the Ginzburg–Levanyuk criterion. Unfortunately, the limited data set does not allow for an estimate of this criterion. One can, however, expect that it will be comparable to that of, for instance, Rb_2ZnCl_4 ($\tau < 10^{-2}$). In the immediate vicinity of the phase transition, the contribution to the anomalies in the thermodynamical quantities due to the defects is expected to be dominant over the contribution due to fluctuations [8].

The values of the critical exponent α have been determined by plotting the data as $\log(k)$ versus $\log(\tau)$, where T_i was defined as the temperature halfway the 'jumps' in the thermal expansion coefficient. For those crystals which exhibit a small maximum above the phase transition, α has been determined from the linear part above this maximum in the $\log(k)$ versus $\log(\tau)$ plots. The resulting critical exponents are tabulated in the fourth column of Table 1. Clearly two types of behaviour are observed. In the compounds which show a relatively sharp phase transition, i.e. the pure chloride compound and the compounds with a high bromide

concentration, α is found to be approximately 0.5. This means that the thermodynamical properties of these compounds can indeed be understood in terms of the order parameter fluctuation correction to the Landau theory. For the low bromide concentration compounds ($x = 0.25$ and 0.45), α is found to be between 0.8 and 0.9. This rather high value of the critical exponent indicates that even far away from the phase transition the influence of defects is not negligible, leading to a renormalization of the critical exponent. In other words, the influence of the defects is still comparable to that of the fluctuations in the order parameter.

Let us now return to Fig. 1. As noted before, the spontaneous deformation already starts to deviate from the observed linear high temperature behaviour several degrees above the incommensurate phase transition. In the pure bromide compound, where the incommensurate phase is absent, this non-linear contribution is found to be much smaller than in the other compounds. The reason for this is probably that long-range elastic forces lead to a suppression of the order parameter fluctuations, and hence to a suppression of the superfluous contribution to the thermal expansion above the ferroelastic phase transition.

The full lines in Fig. 1 show a fit of a $|\tau|^{2\beta}$ behaviour to the experimental data below the phase transition. The resulting fit parameters 2β, tabulated in Table 1, are found to lie within the range 0.64–0.69. The values found for 2β are in good agreement with the exponent obtained by Colla [1] from the temperature dependence of the intensity of a satellite peak in the X-ray diffraction pattern.

It is somewhat surprising that also for the second-order ferroelastic phase transition in the pure bromide compound a value $2\beta \approx 0.7$ is found. From the Landau theory, one would expect to find $2\beta = 1$ for a second-order phase transition. The small value of 2β found for this phase transition is probably due to the proximity of a tricritical point on the ferroelastic phase transition line in the $x - T$ phase diagram of $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$. This tricritical point, where the second-order character of the ferroelastic phase transition changes to a first-order character, should occur because the tricritical point at $x \approx 3.2$ is a triple point and not a Lifshitz point, i.e. the ferroelastic phase transition near the triple point must be of first order, whereas in the vicinity of $x = 4$ it is of second order.

3.2. Thermal expansion near the lock-in phase transition for $x < 0.5$

Upon approaching the lock-in phase transition, the temperature dependence of $\Delta l/l_0$ in the bromide-poor region of the phase diagram starts to deviate from the $|\tau|^{2\beta}$ behaviour found in the central part of the incommensurate phase (see Fig. 1). This deviation might be due to a crossover from a sinusoidal to a soliton-like structure in the incommensurate phase. Another possibility is that the polarization is a secondary order parameter which contributes to the spontaneous deformation. In the compounds with $x < 0.3$, the interaction of the order parameter with the polarization leads to the existence of an improper ferroelastic phase (for which the spontaneous polarization is a secondary order parameter) in a small temperature region. The behaviour of for instance the dielectric anomaly at the lock-in phase transition in the pure chloride compound can be understood in terms of a model which only accounts for a sinusoidal modulation in the incommensurate phase, excluding the existence of a soliton regime [11]. In this model, the interaction of the order parameter $\eta = \hat{\eta} \exp(i\Phi(x))$ with the polarization P in the free energy expansion for $[N(CH_3)_4]_2ZnCl_4$ crystals is described by a $\sigma P \hat{\eta}^5 \cos(\Phi(x) - 2\pi x/15)$ term, where $\Phi(x)$ is a function of temperature. Upon approaching the lock-in phase transition, the polarization increases due to the decrease of the incommensurate wave vector towards its commensurate value, already in the incommensurate phase. This increasing polarization leads to an electrostrictional contribution to the spontaneous deformation ($\Delta l/l_0 \propto P^2$), i.e. $\Delta l/l_0$ should increase faster than $|\tau|^{2\beta}$ upon approaching T_1 the lock-in phase transition temperature. Experimentally, this behaviour is indeed observed in the bromide-poor region ($x = 0.25, 0.45$). For the bromide-rich region, this additional contribution is absent, indicating that in this case the coupling of the order parameter to the polarization is negligible. Although the above analysis does not exclude the existence of a soliton regime in the

bromide-poor part of the x–T phase diagram, it does not provide a strong indication that the incommensurate modulation in these compounds is purely sinusoidal throughout the incommensurate phase.

4. Conclusion

From the analysis in this paper we conclude the following.

In the immediate vicinity of the incommensurate phase transition the behaviour of the thermal expansion coefficient $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$ (smearing out of the phase transition) is caused by the presence of random field type defects.

Somewhat away from the incommensurate phase transition ($T \geqslant T_i + 3$ K), where it is expected that the defects contribution is smaller than the contribution resulting from the order parameter fluctuations, the temperature dependence of the thermal expansion coefficient for the compounds with $x = 0, 2.4, 2.9$ can be described by a τ^{α}-dependence with $\alpha \approx 0.5$. However, for the chlorine-rich compounds ($x = 0.25, 0.45$) a value of $\alpha = 0.8 - 0.9$ has been found, strongly suggesting that in this case the defect contribution remains important even away from the phase transition.

The spontaneous deformation in the low temperature part of the Incommensurate phase of the chlorine-rich compounds upon approaching T_1 shows a faster increase than $\tau^{2\beta}$. This possibly results from a coupling of the order parameter to the polarization.

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